BRINE LEACHING OF LEAD-SILVER ORES, WITH ELECTROLYTIC PRECIPITATION

A

THESIS

SUBMITTED BY

ROBERT D. BRADFORD

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE IN METALLURGY

UNIVERSITY OF UTAH

SALT LAKE CITY

1925

Approved _____

TABLE OF CONTENTS

by

E. F. Newton*, G. L. Oldright**, and Robert D. Bradford***

* Assistant Director of Research, Dept. of Metallurgical Research, University of Utah.
** Hydrometallurgist, U. S. Bureau of Mines, Intermountain Station.
*** Research Fellow, 1924-25, Dept. of Metallurgical Research, University of Utah.

INTRODUCTION.

The present economic importance of lead has greatly emphasized the necessity of obtaining it from its low grade ores. Recent developments in flotation have simplified very much the problem as regards sulphide ores, but other methods must be employed when oxidized lead ores are encountered. In most of the low grade deposits, silver in varying quantities is present, so that when developing a method of extracting the lead the silver extraction must also be considered. Ordinary concentration methods are not applicable to such ores and therefore other processes must be perfected.

The direct smelting of these ores is unprofitable. The smelters will not pay for lead in ores carrying less than 4 to 5 per cent. They calculate the treatment charge plus their profit at between $10 and $14 per ton. One large mining company has designated as the critical lead-silver content determining whether an ore may be smelted or milled, as 4.5 to 5.5 per cent lead and about 30 ounces silver. This is calculated from the following formulae.

Smelting-- (ounces Au) x $19 + (.95 x .95 x ounces Ag x .67)

- $7.75 (freight and treatment)

= Returns.

Milling-- (.80 x .95 x ounces Ag x .67) + [.30* x (lb. per ton Pb) x .07]

- (3.5 ÷ .67)

= Returns.

Therefore those oxidized ores that cannot be treated by flotation, whose lead content is too low to be paid for by the smelters and whose precious metal content is insufficient to meet smelter charges, must be treated in other ways.

Ores of this type having an acidic gangue, that is, ores containing bases in sufficiently small amounts to be neutralized by SO_4 in roasting, with enough extra sulphides to ensure good chloridising, and sufficient acid for leaching, are amenable to treatment with acidified brine. It was on ore meeting these specifications that the following work was done.

BRINE LEACHING PROCESS.

In the use of the brine leaching process, the brine solution used as the solvent must be kept acidified in order to prevent the formation of basic lead precipitates and to recover satisfactory amounts of the silver. As stated above, this limits brine leaching to siliceous ores. Before attempting to leach, it is preferable that the silver and lead both be present in a readily soluble form; either as a sulphate or chloride. For most ores, roasting assists the formation of these compounds, or others less desirable, but still soluble. Messrs. Holt and Dern designed a blast roasting furnace for giving such

*Lead recovery-- it may be increased from 30 to about 90 per cent.

a roast, and contributed to the development of a leaching process to handle the roasted product. Some of the steps in the process need perfecting and it was the purpose of this research to determine means whereby this could be done. However, before going into the discussion of the research investigation, a brief description of the Holt-Dern process will be given.

HOLT-DERN PROCESS.

Roasting.

The Holt-Dern furnace is a blast type roaster and consists of a steel rectangular shell holding about five tons of charge in a bed some 30 inches deep. The fuel is mixed with the charge and the blast is applied at the bottom. The furnace operates on a batch system, the roasted product being discharged at intervals by rocking a series of pivoted arc grates at the bottom of the charge.

The low grade of the ore necessitates low cost of treatment. The above furnace furnishes a cheap means of chloridizing roasting, because of its low first cost and the small amount of fuel necessary. However, it has its limitations. First, it is limited to small tonnages due to its small capacity; second, the amount of labor necessary to charge and level the ore is large; and third, in order to have even distribution of the blast, the ore must be crushed in stages and screened.

Leaching.

The solubilities of lead and silver sulphates or chlorides depend upon the concentration of the chlorides in the brine. In dilute brines, the solubilities of the lead salts are less than in pure water, but in strong brines the solubilities are much greater. Results of M. Demassieux* on the solubility of lead chloride are shown in Figure 2. The effect of temperature can be observed from the figure. The points at the breaks in the curves, to the extreme right, represent the maximum concentration of NaCl and $PbCl_2$ which can exist at the corresponding temperatures. To the right of these points the curves represent solutions saturated in NaCl but with varying $PbCl_2$ concentrations. If $PbCl_2$ be added to the solutions, some NaCl will be thrown out until the composition represented by the points at the breaks are reached. The chlorides of copper and silver act much the same as that of lead, giving curves similar to those of Figure 2.

The curves show that the leaching solutions should be kept at a concentration near saturation, and the temperature kept reasonably high in order that a satisfactory amount of the valuable metals may be soluble in a given volume of solution.

Uneven roasting results in the retention of unaltered sulphides, from which the silver and lead will not be dissolved. However, the unaltered mineral may be made soluble by the introduction of an oxidizing agent. The most easily obtained and

*M. Demassieux, Comt. Rendus (1914) 158, 702.

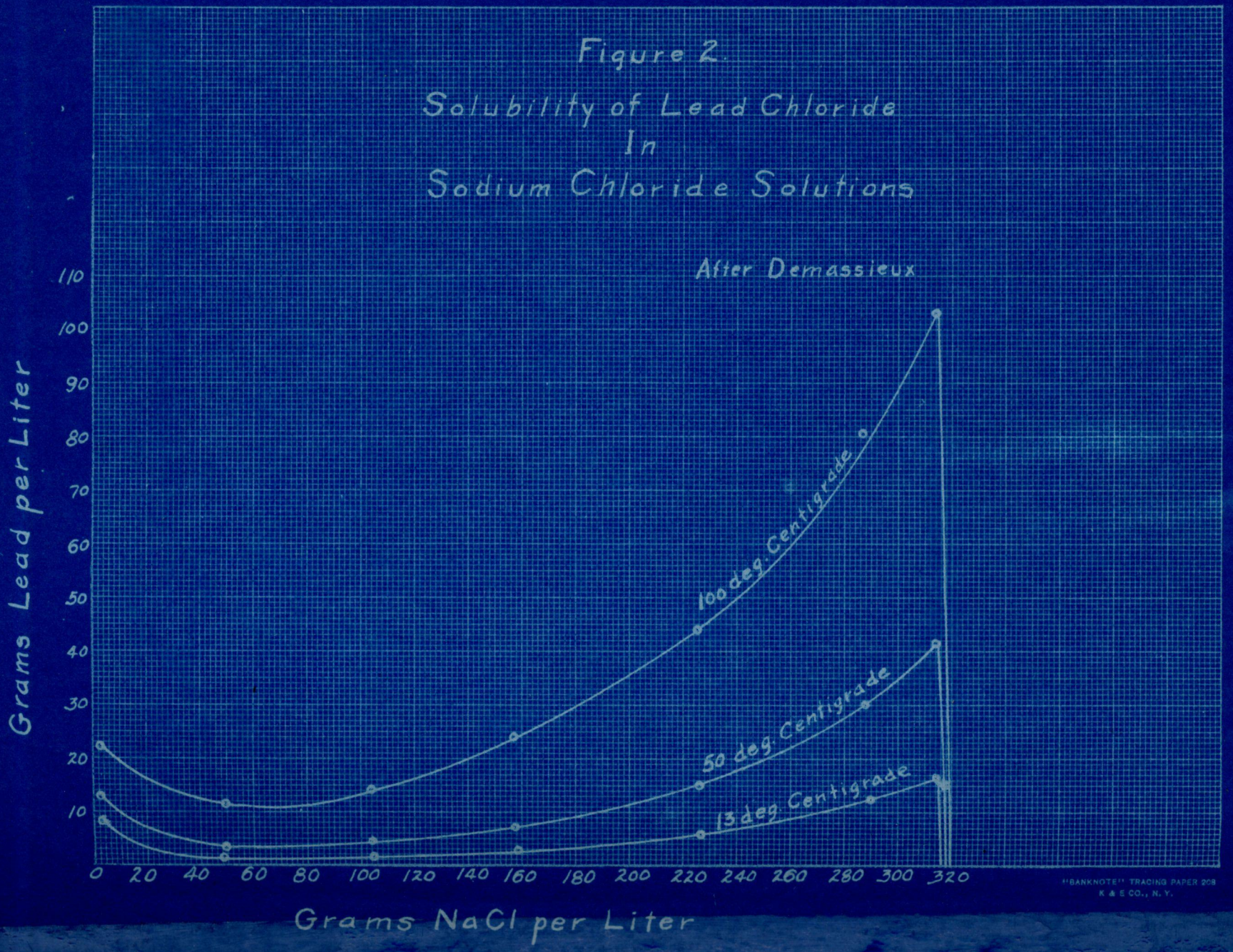
Figure 2.
Solubility of Lead Chloride
In
Sodium Chloride Solutions
After Demassieux
Grams Lead per Liter
110
100
90
80
70
60
50
40
30
20
10
100 deg. Centigrade
50 deg. Centigrade
13 deg. Centigrade
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320
Grams NaCl per Liter
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and cheapest oxidizing agent is some ferric salt, ferric chloride being particularly advantageous for our use.

Precipitation.

In the Holt-Dern process the metals are precipitated from solution as follows: The silver is precipitated by the addition of finely divided cement copper in air agitation (Pachuca) tanks. Next the copper is precipitated on scrap iron, and finally the lead is precipitated on fine strips of detinned "canner's" scrap. The silver and copper can be almost completely precipitated at room temperature, but the lead requires a hot solution or an undue length of time of contact of the solution with the scrap iron.

The amount of solution in the circuit is sufficient to dissolve all the lead from the roast if the solution be barren of lead at the start of the leach. However, if after precipitation the barren solution still contains about half its carrying capacity of lead, and it then be used as the leach solution, only 50 per cent of the lead can be dissolved unless larger volumes of solution are circulated.

OBJECT OF THE EXPERIMENTS.

From the above description of the brine leaching process, the objects to be achieved by experimentation in an effort to improve the process, may be summarized as follows:

1. To provide a cheap oxidizing agent in the leaching solution so that the unaltered mineral in the roast may be dissolved.

2. To precipitate the lead more completely from solution, i.e. to secure a barren solution from the lead precipitation boxes so that the amount of lead to be again taken up in the leaching vats will be a maximum.

3. To be able to treat ore crushed more cheaply; to remove the necessity for stage crushing with intermediate screening, and also to treat ore which has been roasted on a larger scale in a more cheaply operated furnace. If possible, to treat ore roasted without the addition of a chloridizing agent (Na Cl).

Acknowledgment.

The writer is greatly indebted to Mr. G. L. Oldright, Hydrometallurgist, Intermountain Experiment Station of the U. S. Bureau of Mines, under whose immediate direction this work has been done. His many suggestions have been invaluable. Credit is likewise due Dr. R. F. Newton, Director of Research, Metallurgical Research Department of the University of Utah, for his assistance, and to the Tintic Standard Mining Company for hearty cooperation in the investigation.

EXPERIMENTAL WORK.

Electrolytic Lead Precipitation.

Since the ordinary method employed in commercial practice of precipitating the lead, (i. e. by deposition on scrap iron in hot solution) has failed to give good results, the precipitation by electrolysis was suggested.

In developing a suitable electrolytic cell two points were kept in mind. The first was to obtain a barren solution (to precipitate all the lead) and at the same time to secure a high current efficiency. The second was to make use of the oxidation which takes place at the anode in such a way as to generate an oxidising agent in the barren solution as previously mentioned. By the use of a diaphragm cell with an insoluble anode, these two points can be attained. As the lead is precipitated at the cathode the solution is oxidised at the anode. The amount of lead precipitated at the cathode and the amount of iron oxidized at the anode depends upon the cathode and anode current efficiencies. The diaphragm must be of material which will prevent mechanical mixing of the catholyte and anolyte but will at the same time offer little resistance to the passage of the electric current.

To obtain a high cathode current efficiency with almost complete lead precipitation, the catholyte must be vigorously agitated. The vigorous agitation is necessary because the solution of low lead concentration adjacent to the cathode is very quickly depleted of lead and unless fresh solution be quickly furnished in the immediate vicinity of the cathode, hydrogen will be evolved. With good stirring the solution next to the cathode is kept comparatively high in lead, and a good current efficiency results. Another reason for the need of agitation of the cathode is that it is highly probable that in the concentrated brine solution, complex ions are formed. Lead and chlorine may combine to form a

complex ion having a negative charge, and the lead may therefore migrate towards the anode. However, if by agitation the ions are brought into contact with the cathode the complex ions will be broken down and the lead be precipitated as metal.

Experimental Cell.

Figure I is a drawing of the experimental cell showing a cross-sectional view. The sides of the cell are of soft wood and the corners and edges are sealed on the inside with paraffin. The anode is of graphite, cut from a large furnace electrode. The diaphragm used is set in grooves in the sides and bottom of the cell and is also sealed with paraffin, so as to be leak proof. The cathode is made from a sheet iron disk. It is revolved by means of a steel shaft which passes through the side of the cell. Four baffles are set radially on the disk, and are spaced at equal angles. They are set at right angles to the plane of the cathode and are nearly 5/8 of an inch in width. The electrical connection to the anode is made from a copper wire which is inserted in the graphite. The cathode connection is made by means of an iron disk attached to the revolving shaft which has its circumference in contact with mercury. From the mercury the connection is made by use of a copper wire fastened to the bottom of the mercury container.

Laboratory Tests.

On account of the large amount of solution necessary to carry on the laboratory experiments, and the amount of work required to prepare it in our laboratory, the solution for our tests was

obtained from the mill of the Tintic Standard Mining Company at Harold, Utah. This company operates a mill of 250 tons daily capacity using the Holt-Dern process, and they have cooperated whole-heartedly in the prosecution of this work. The solution obtained is called at the mill, "the lead box heads." It is the pregnant solution which has had the silver and copper removed, being pregnant only in lead. The following is a partial analysis of the solution.

TABLE 1.

Lead	7-10 gr. per liter	Ferric Iron	0.38 gr. per liter
Copper	0.167 gr. per liter	Insol.	0.137 gr. per liter
Total Iron	16.75 gr. per liter	Sulphate	31.7 gr. per liter
Specific Gravity	1.22	Chlorine	170.0 gr. per liter
Zinc	4.31 gr. per liter	Acid	0.02 gr. per liter

From the above analysis it can be seen that some purification of the solution should be made before attempting to electrolyze. The small amount of copper present should be removed so as to obtain a high grade electrolytic lead. Also the ferric iron should be reduced so as not to use electrical energy for such a purpose. Therefore, prior to any electrolysis experiments, tests were made to determine means of purifying the solution.

Purification Tests.

The first method tried in the purification experiments, was the use of hydrogen sulphide. A given amount of solution was

treated with hydrogen sulphide in excess of that required for complete precipitation of the copper. Lead sulphide was formed readily, and it was thought that the PbS would then displace any remaining copper by precipitating it as Cu_2S and the lead would again go into solution. However, such was not the case. After treatment with hydrogen sulphide, the amount of copper in the solution was the same as before. This is probably due to the presence of ferric iron in the solution which is capable of dissolving the cuprous sulphide, especially in the presence of the strong brine.

The next purification method experimented with, was the use of lead amalgam as a precipitant. A given amount of solution was placed in a long vertical tube and the lead amalgam was allowed to fall in a very finely divided state through the column of solution. Samples of the solution were taken at intervals. The ferric iron soon disappeared and the copper was then almost completely removed. In the amalgam the copper replaced the lead, and after being used for some time the mercury became semisolid due to the accumulation of copper. The copper amalgam was then retorted, thus obtaining metallic copper. It was determined by calculation that in practice an excessive investment would not be required for the mercury, and that the expense for this material would not be large.

Since in the lead amalgam, the function of the mercury was primarily to permit the fine subdivision of the lead, experiments were later performed using the spongy lead precipitate from

the electrolytic cell. A quantity of solution was heated to the temperature corresponding to that used at the Tintic Standard Company's mill for precipitation of the lead, and some lead precipitate was added and the solution stirred. At the temperature of 70° C. and with a slight excess of lead, the copper was almost completely precipitated in about 30 minutes.

The purification experiments show that by using the electrolytic lead precipitate the copper can be quickly, easily and almost completely removed, and the ferric iron reduced, if the solution be heated to a reasonable temperature, say from 50 to 80° C. The rate of precipitation depends upon the temperature of the solution and the amount of surface of the lead exposed.

Electrolytic Tests.

In all the electrolytic tests, the composition of the solution was practically that given in Table 1, and the small amount of copper present was not removed. Therefore the resulting lead precipitate carried some copper; however, the amount present in the solution was so small in comparison with that of the lead, that in calculations of current densities it could be neglected.

The cathode and anode compartments of the cell held 1000 c.c. each. This brought the solution level just to the top of the cathode. (See Figure I.) In all the experiments the

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reverse side of the cathode, that not having the baffles, was paraffined. The solution placed in the anode compartment was the exhausted catholyte from the previous test, it being barren of lead; this would correspond in plant practice to running the pregnant solution through the cathode compartment to precipitate the lead and then running the resulting reduced, barren solution through the anode compartment to oxidize the ferrous chloride. The current was measured by means of an ammeter placed in the circuit and the voltage was measured by connecting a voltmeter across the cell. Both meters were checked against precision instruments in the Electrical Laboratories of the University of Utah. The source of the current was four storage batteries, capable of furnishing from 250-300 ampere hours at from 8 to 9 volts. The current density was determined by dividing the ammeter reading by the square feet of cathode area exposed to the solution. The current efficiency at a given concentration of lead in the solution was determined by computations from analysis of samples of solution taken at regular intervals, then determining the amount of lead precipitated in a given interval and comparing the amount precipitated with that computed by Faraday's Law.

Experiments were conducted to determine the effect on the current efficiency of varying the current density, the rate of catholyte agitation, and the lead concentration. Each set of tests is shown by the different curves which follow.

Explanation of Curves.

Figure 3 shows the change in current efficiency with varying speeds of cathode rotation. The efficiency is expressed in per cent and the degree of agitation in revolutions per minute of the cathode.* The current density was kept constant at 30 amperes per square foot of cathode area. Each point on the curve represents a separate test. With no agitation the current efficiency is about 20 per cent and as the agitation increases the efficiency also increases until between 70 and 75 r.p.m. the efficiency is near its maximum, about 98 per cent. Therefore with a current density of 30 amperes per square foot the cathode should be revolved at about 75 r.p.m. to keep the current efficiency as high as possible.

Figure 4 shows the change in current efficiency with varying current density. Each curve represents a constant amount of agitation, going from no agitation in the lower curve to 75 r.p.m. in the upper one. They all show that as the current density increases the efficiency falls off. Thus, as stated above, for 75 r.p.m. the agitation is sufficient to give high current efficiency with 30 amperes per square foot, but if the density be increased the efficiency decreases. Therefore, all the curves of Figure 4 show that the agitation must be increased as the density is increased in order to keep a high current efficiency.

*Note: Since there are no generally accepted units of agitation, revolutions per minute of the cathode will be the units employed in this discussion.

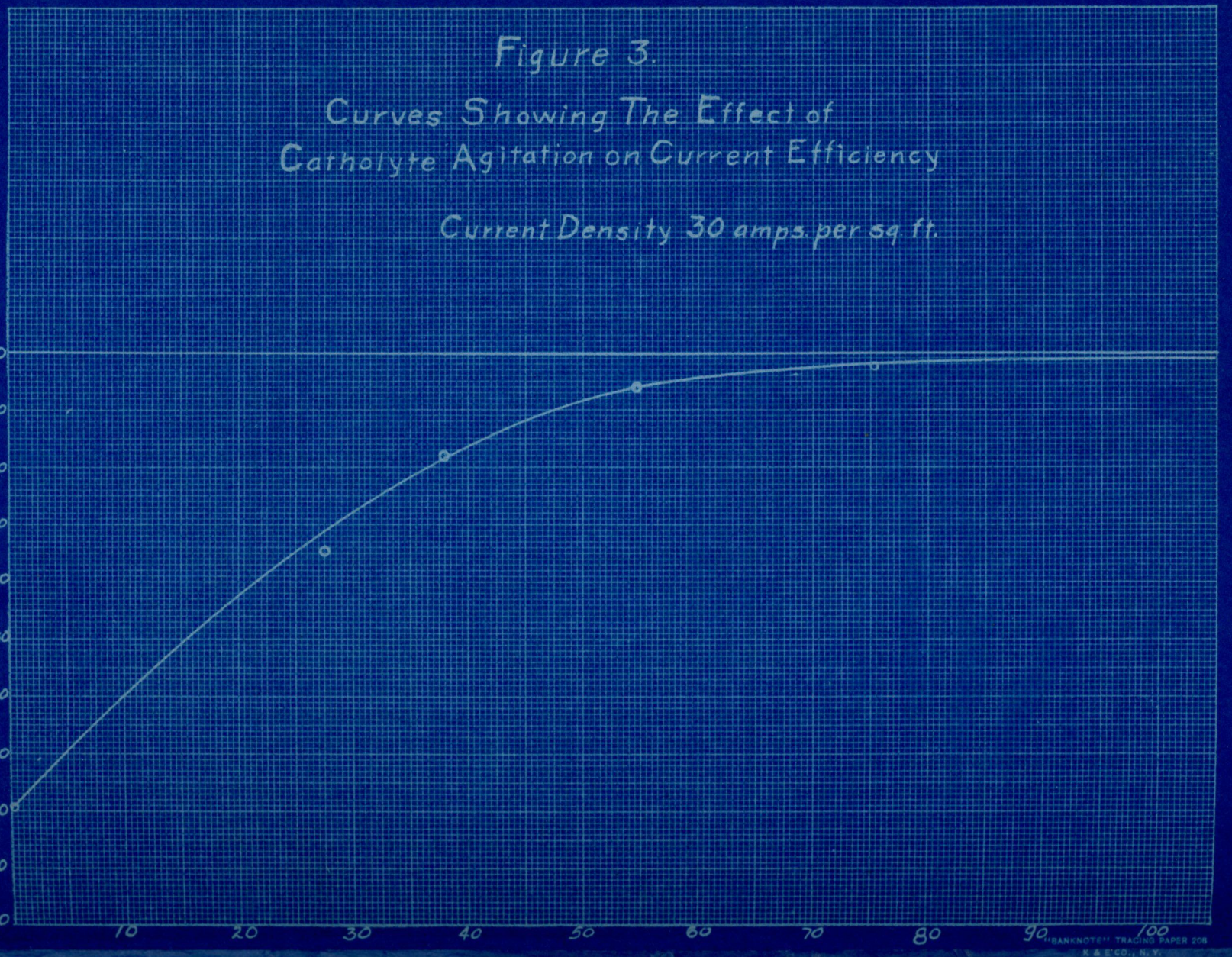
Figure 3.
Curves Showing The Effect of
Catholyte Agitation on Current Efficiency
Current Density 30 amps. per sq ft.
Current Efficiency / per cent
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
Catholyte Agitation cathode rev. per min.
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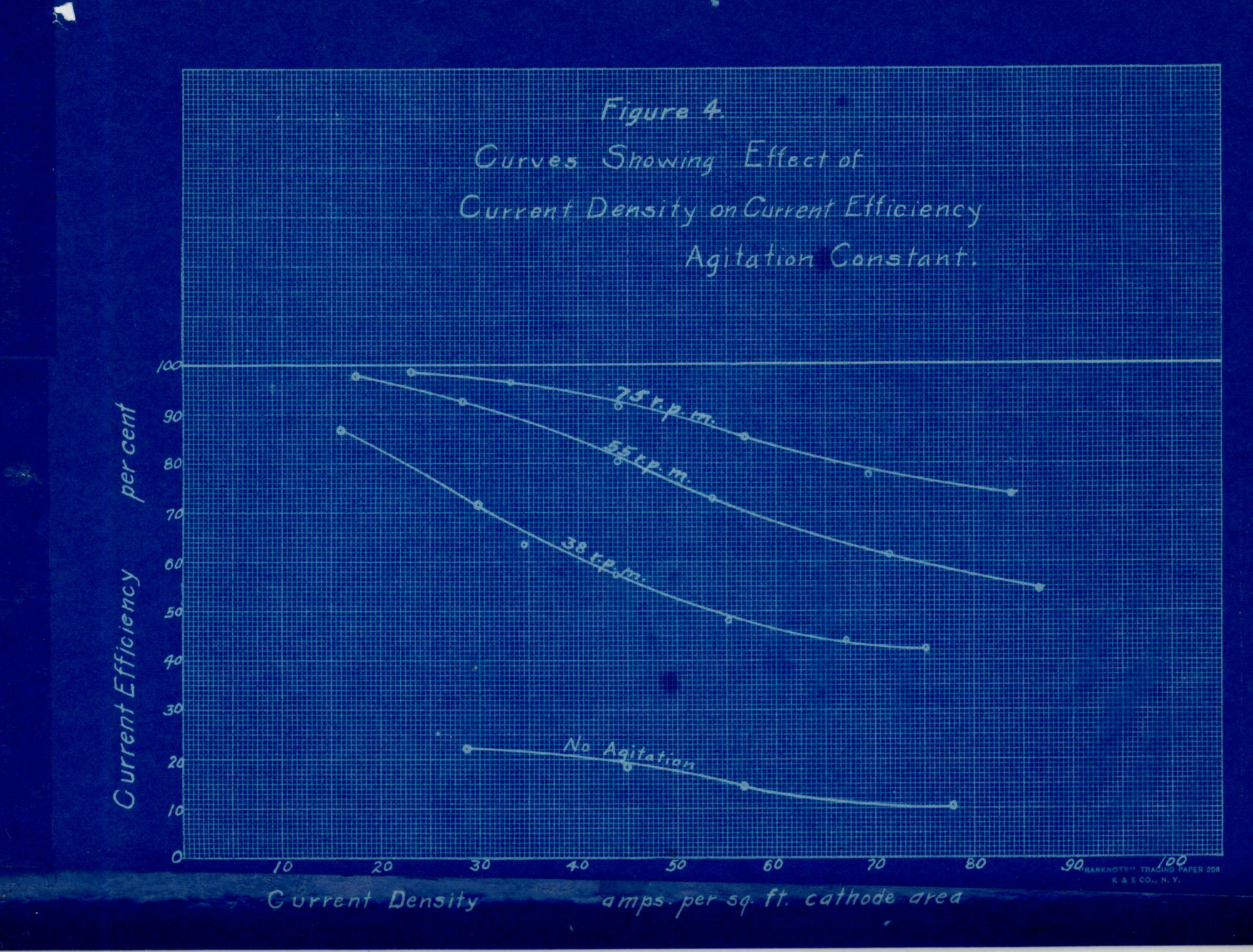
Figure 4.
Curves Showing Effect of
Current Density on Current Efficiency
Agitation Constant.
Current Efficiency per cent
100
90
80
70
60
50
40
30
20
10
0
75 r.p.m.
55 r.p.m.
38 r.p.m.
No Agitation
10
20
30
40
50
60
70
80
90
100
Current Density amps. per sq. ft. cathode area
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Figure 5 shows the change in current efficiency with the change in lead concentration of the catholyte, the current density and rate of agitation being kept constant. The upper curve represents a test made with current density of 30 amperes per square foot and a rate of agitation of 75 r.p.m. The vertical dotted line shows the original concentration of the lead in the pregnant solution at the beginning of the test. The ordinate for any point on the plotted curve gives the mean current efficiency for that concentration obtaining at the start of the test, to that given by the abscissa of the point in question.

The lower curve represents data similar to those shown by the upper one, except that the concentration of the lead was lower at the start and the rate of agitation was decreased to 38 r.p.m.

Figure 6 shows the increase in voltage across the cell with increasing current density.

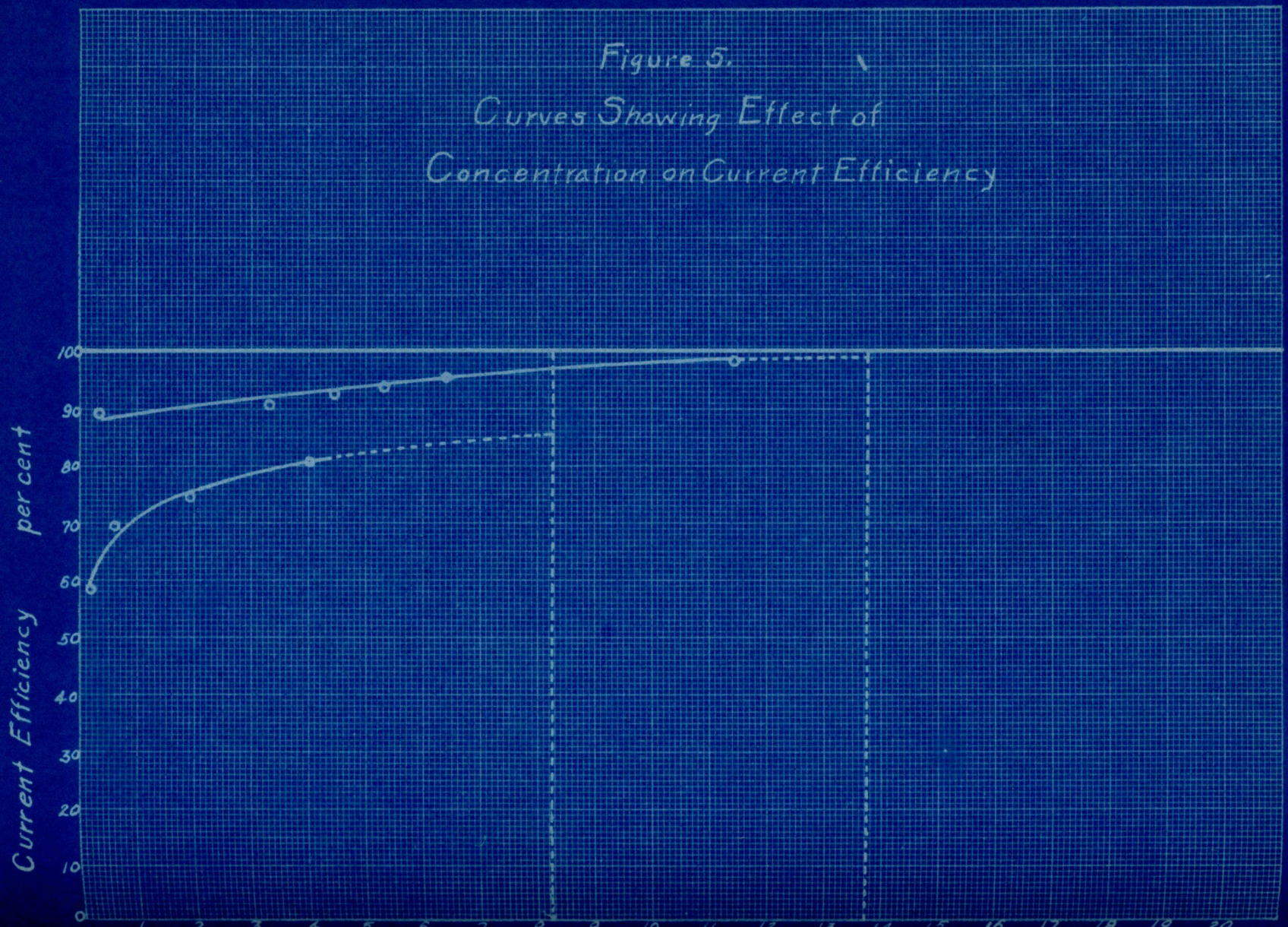
Anode Reactions.

All the above curves and discussion have dealt with the cathode compartment of the cell and the precipitation of the lead. Little has been said about the anode compartment other than that the iron in the barren solution is oxidized to the ferric condition. As the solution is withdrawn from the cathode compartment the spongy lead precipitate is settled and removed, and the solution placed in the anode compartment. As the current is applied to the

Figure 5.

Curves Showing Effect of

Concentration on Current Efficiency



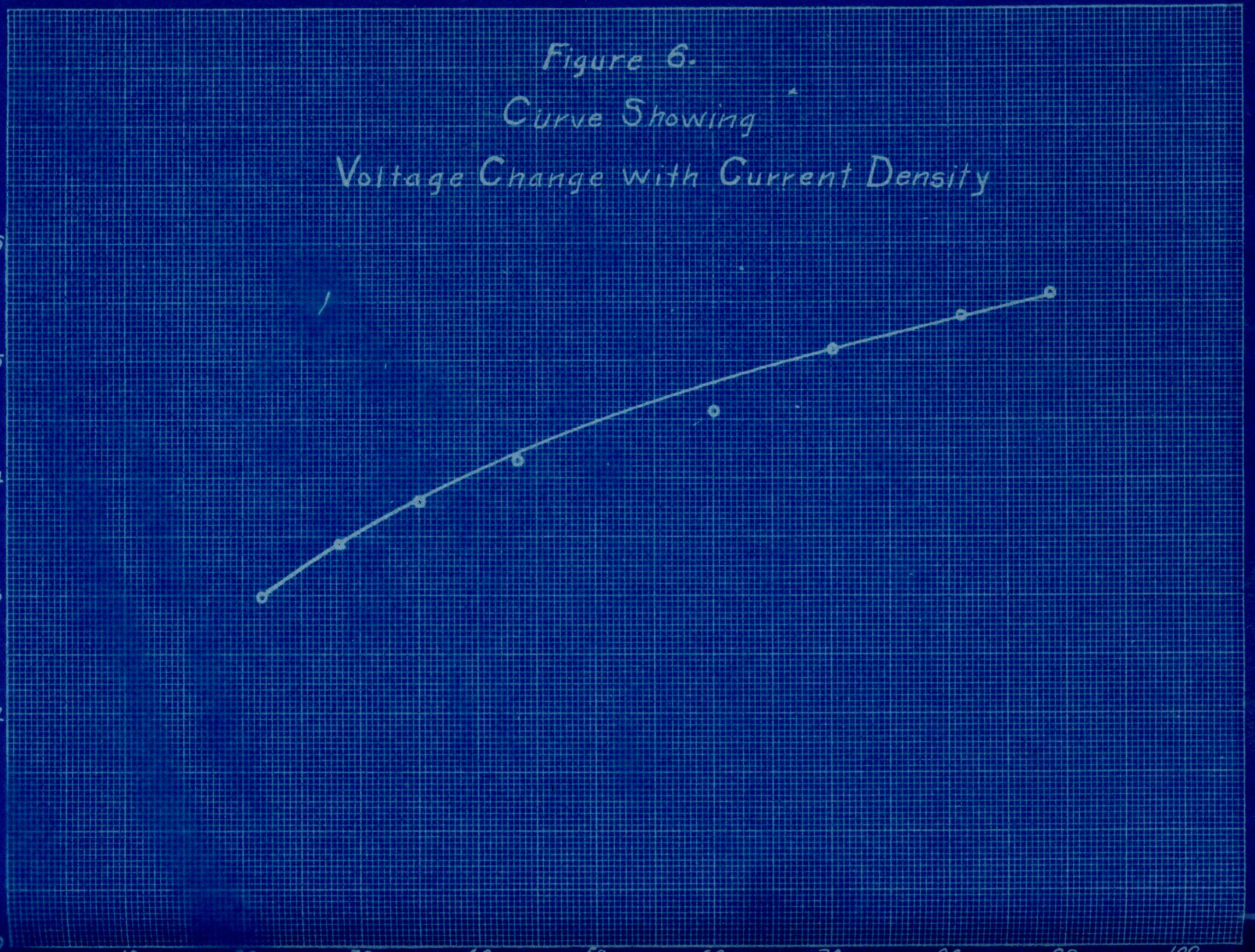


Figure 6.
Curve Showing
Voltage Change with Current Density
Voltage across Cell Volts
0
1
2
3
4
5
6
10
20
30
40
50
60
70
80
90
100

cell the iron is rapidly oxidized. No agitation is provided for the anolyte so that at the higher current densities as the iron was oxidized some chlorine gas ~~was~~ is formed. However, under these conditions the completeness and speed with which the iron is oxidized is remarkable.

At the conclusion of the test the anolyte is removed and stored for future use as a solvent in the leaching experiments. The lead precipitate is also saved until sufficient quantity is on hand to warrant melting it into a bar. Preliminary to melting, the precipitate is washed well and dried. Care must be taken in drying since the spongy lead oxidizes readily. The following is an analysis of some of the melted lead precipitate.

TABLE 2.

Silver	2.5 ounces	Sulphur	Nil.
Zinc	Trace ?	Iron	Nil.
Copper	5.98 per cent	Lead	92+ per cent.
Arsenic	1-2 per cent ?		

LEACHING TESTS USING OXIDIZED BRINE.

Leaching tests were performed on ore roasted with and without salt, and on raw ore. The raw ore and chloridized calcine were obtained from the Tintic Standard Mining Company's mill. The oxidizing roasts were made in our laboratory from the raw ore.

Tests on Chloridized Calcine.

The chloridized calcine was prepared in a blast type (Holt-Dern) roaster and as has been stated ~~in an~~ earlier ~~part~~, it contained some unaltered ore. Mineralogical analysis by means of the microscope to determine the form in which the silver and lead are present in the roast and to obtain quantitatively the amount of unaltered mineral, were attempted but with no positive results. It is very difficult to identify colorless or light colored oxidized material in a badly weathered rock; sulphide minerals themselves may easily be distinguished. The Tintic Standard mine is known as a mineralogical curiosity shop in the variety of minerals present. It is particularly difficult to identify in an ore of this type minerals that occur in such small amounts as do those of silver.

The following is a chemical analysis of the chloridized calcine used in the experiments.

TABLE 3.

Gold	0.04 ounces	:	Iron	1.5 per cent
Silver	14.34 ounces	:	CaO	Nil.
Lead	3.12 per cent	:	Sulphur	1.5 per cent
Copper	0.10 per cent	:	Insol.	62.8 per cent

As the calcine leaves the furnace it is sintered, porous, and suitable for leaching by percolation. However, in carrying on the laboratory tests, the leaching was done in two

liter acid bottles agitated by being turned on two parallel rolls. The rolls were kept in a closed, electrically heated hood, thus enabling one to keep the temperature nearly constant and above that of room temperature. At the Tintic Standard mill the leaching is done in acid proof concrete vats and the temperature of the solution is kept at from 50 to 70° C. In all brine leaching the temperature has great effect on the rate of dissolution of the lead and silver. In the laboratory tests the temperature of the leaching solution was somewhat below the above figures, and varied from about 40 to 50° C.

Table 4 shows the data from some of the tests performed on the chloridized calcine. The calcine used in all cases was of the above composition and the leach liquors were nearly saturated in NaCl. They had a specific gravity of about 1.23 and contained the amount of ferric iron shown in the table. Sufficient acid was kept in the solution to prevent the hydrolysis of the ferric salts.

TABLE 4.

No.	Time of Agitation	Temp.	Pulp Ratio	G.P.L. Ferric Iron Preg. Sol.	Anode Sol.	Per Cent Ag Ext.	Pb Ext.
1	2 Hrs.	42°C.	4:1	2.0	2.7	68	83
2	4	45	4:1	2.0	2.7	69	85
3	8	45	4:1	2.0	5.0	83	83
4	14	48	4:1	2.04	5.2	88	96
5	24	50	4:1	2.05	5.8	88	95
6	48	45	5:1	3.17	6.0	90	97

All of the tests show that excess ferric iron was present in the leaching solutions since there still remains ferric iron in the pregnant solution. The degree of the extraction of both the lead and the silver does not change much after agitating for a time greater than 14 hours. In some additional tests the pulp ratio was varied from 3 to 1 to as high as 6 to 1 but this seemed to have little effect on the extraction. The 4 to 1 pulp ratio was used because it agrees closely with the ratio used in commercial practice.

To determine the advantage of the use of the oxidized anode solution in bettering the extraction from the chloridized calcine, tests were made using brine without the addition of any oxidized iron whatsoever. Results of a few of these tests are shown in Table 5.

TABLE 5.

No.	Time of Agitation	Temp.	Pulp Ratio	Per Cent Ag Ext.	Per Cent Pb Ext.
1	2 Hrs.	50°C.	4:1	57	91
2	4	54	4:1	59	91½
3	20	50	4:1	63	93
4	24	50	4:1	69	92

Comparing test No. 3 of Table 5 with tests No. 4 and 5 of Table 4, the time of agitation for the first test is seen to be between that required by the last two ~~is the same for each one~~. The ~~oxidized~~ brine gives only a little better lead extraction but ~~not nearly~~

page 18(a)

The ~~additional~~ increased solvent action caused by the addition of ferric chloride to a synthetic brine solution may be seen by comparing tests 4 and 5, table 4, with test 3, table 5, both sets of tests being made with saturated brine, but ferric chloride being added to the tests shown in table 4. The time of treatment of the ore with the brine alone lies between that given the two samples treated with ferric chloride in addition, and the temperature in all cases was nearly the same. The addition of ferric chloride ~~assists~~ improves the ~~dissolving~~ recovery of lead only ~~some two per cent~~ slightly, but increases the extraction of silver 25 per cent.

page 18(a)

~~as good~~ a much better silver extraction. ~~The decreased lead extraction undoubtedly is due largely to the temperature difference, the former test being at 50° C. while the later was at 42° C.; rather than that the ferric iron has any retarding effect. However,~~ In case of the silver extraction the presence of ferric iron in the leaching liquor greatly improves the extraction, even with the adverse temperatures. This indicates that the lead in the chloridized calcine is easily soluble in the unoxidized leaching solution and that the addition of an oxidizer helps but little; while in the case of the silver the presence of an oxidizer greatly improves the extraction.

The above phenomena are partly explained from the known degree with which the lead and silver can be converted to sulphate or chloride when roasted. The lead sulphatizes and chloridizes readily while the silver does not, and after the sulphate and chloride of either metal is formed the presence of an oxidizer in the brine solution will help little in bettering the extraction.

From the tests performed on the chloridized calcine it can be said that: first, the presence of ferric chloride in the leaching solution is advantageous in increasing the silver extraction, but that the lead is soluble in the unoxidized brine; and second, that in using ferric chloride in the solution the acid strength must be maintained sufficiently high so that the iron will not be precipitated as the hydroxide.

LEACHING TESTS ON RAW ORE.

The raw ore obtained from the Tintic Standard mill was

that which had been mixed with about 10 per cent of salt (sodium chloride) and crushed to the degree of fineness for the Holt-Dern furnaces. In the experiments performed all weights were taken of the ore-salt mixture and all extraction calculations were made from the assay of the mixture. However, a few tests were made on the raw ore after the NaCl had been washed out.

The following is a partial analysis of both the raw ore containing salt and the washed raw ore.

TABLE 6.

	Ag oz.	Pb %	Cu %	Zn %	S (total) %	S % Sulphate	CaO %
Raw Ore - NaCl Mixture	14.85	4.52	-	-	-	-	-
Raw Ore	17.34	5.20	0.30	0.12	2.5-4.0	0.52	0.30

Laboratory Procedure and Results.

Tests were performed in the same manner as those on the chloridized calcine. The temperature of leaching was kept at nearly 45° C. and the agitation was effected as before, by the use of bottles placed on a roller agitator. The leaching solution used was the oxidized ~~anode solution~~ anolyte from the electrolytic cell.

The following table shows data from some of the tests. As a means of comparison test No. 7 was added to show the extraction using no oxidized iron in the leach liquor.

lead with these elements, forming insoluble compounds. More will be said as to this supposition in the discussion of the work which follows on oxidized roasts.

LEACHING TEST ON OXIDIZED ROASTS.

As was stated in an earlier portion of the thesis, one of the objects of the investigation was to determine whether or not with an oxidized leaching solution, a good extraction of the lead and silver could be obtained by giving the ore a cheaper roast without the addition of a chloridizing agent. In performing tests of this nature, the raw ore to be roasted was washed thoroughly to remove all the NaCl and then dried and analyzed. The analysis was given in Table 6.

The roasting was carried out by placing the ore in a clay dish and heating in an electrically heated muffle. The temperature of roasting was closely controlled and was measured by the use of a pyrometer. The hot junction of the thermocouple was kept inserted in the roast. After the roast was finished it was cooled and a sample was taken for analysis. Table 8 gives the analysis of a number of different oxidized roasts.

TABLE 8.

No.	Roasting Temp.	Ag oz.	Pb %	Total S %	Sulphate S %
1	220°C.	17.28	5.07	2.29	0.66
2	450	17.30	5.20	1.53	1.43
3	500	16.85	4.92	1.46	1.42
4	600	16.82	4.95	1.25	1.12
5	700	16.70	4.87	1.41	1.32
6	770	16.35	4.80	1.09	1.06
7	825	18.25	4.70	1.06	0.99

Note: Time of roasting was 1½ hours.

Each roast was leached with oxidized anode solution. The time of leaching was maintained at from 20 to 24 hours, since from the previous tests the action of the oxidized iron seems to be fairly rapid, and there was no advantage in longer time of contact. The ferric iron in the leaching solution was kept in excess and sulphuric acid was added to furnish the necessary acidity. From the data obtained the silver and the lead extraction was determined for each roast, and in Figure 7 the extraction has been plotted against the temperature of roasting.

The upper and lower curves show the changes in lead extraction and in silver extraction, respectively, with the change in the temperature of roasting. The lead and silver

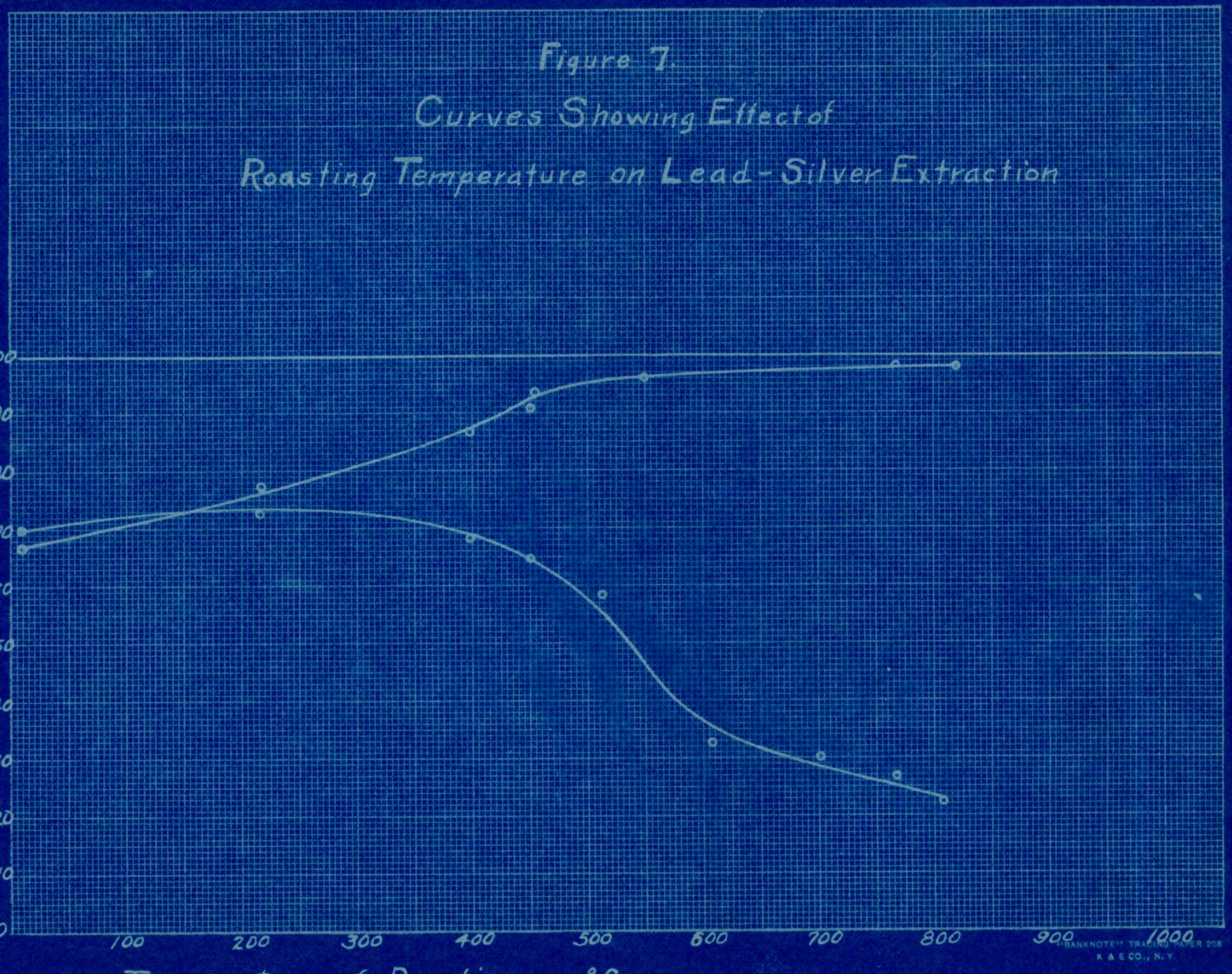


Figure 7.
Curves Showing Effect of
Roasting Temperature on Lead-Silver Extraction
Per cent Extraction
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
500
600
700
800
900
1000
Temperature of Roasting °C
"BANKNOTE" TRACING PAPER 208
K & E CO., N.Y.

extractions from the raw ore are about 67 and 70 per cent respectively, as is also shown in Table 7. As the ore is roasted at higher temperatures the lead extraction gradually increases until the sulphatising temperature interval is reached — from 400 to 500° C. Here the extraction rapidly increases until near 600° C. it is almost a maximum. However, the silver behaves very differently. The extraction stays nearly constant as the temperature of roasting increases until the temperature of 400° C. is reached. From this temperature to 600° C. the extraction rapidly decreases from near 67 per cent to about 35 per cent. From 600° C. to 825° C. the extraction still continues to decrease though more slowly, being only about 22 per cent at the latter temperature.

Explanation of Data.

The increase of lead extraction with higher roasting temperatures is almost certainly due to the formation of lead sulphate or perhaps lead oxide, which can readily be dissolved. The insoluble compounds in which the other 30 per cent of the lead occurs in the raw ore, are broken down as the temperature is increased, and nearly all the lead has become soluble at a roasting temperature of 600° C.

The silver curve cannot be so readily explained. At the temperature where the lead extraction increases, the silver extraction decreases so that instead of soluble compounds forming, insoluble compounds result.

At the higher temperatures some silver minerals may decompose and give metallic silver. If metallic silver were only slightly dissolved by the leaching solutions such reactions (or such a reaction) might explain the decrease in the silver extraction with increased roasting temperature. To test this supposition, a sample of pure silver foil was weighed and placed in a flask with some of the oxidized leaching solution. After remaining in the solution at room temperature for about 48 hours, the remaining silver was removed, washed and weighed. It was found that a considerable amount of the silver had been dissolved. In fact the silver concentration of the solution was greater than the silver concentration in the ordinary pregnant solutions. This immediately disproved the supposition that the formation of metallic silver accounts for the decreased silver extraction.

The next explanation advanced was the formation, at higher roasting temperatures, of compounds of silver and arsenic or antimony which might be insoluble in the oxidized brine. To test this explanation, pure compounds of silver and arsenic were prepared and their solubility determined. The yellow silver arsenite (Ag_3AsO_3) was prepared by precipitating it from a solution of As_2O_3 by the addition of silver nitrate. The red silver arsenate (Ag_3AsO_4) was also prepared by fusing equal parts of KNO_3 and As_2O_3, dissolving the resulting mass in water, and precipitating the salt by adding silver nitrate.

Samples of the silver arsenite and arsenate were weighed and placed in flasks with the oxidized leaching solution. Other samples of each were placed in porcelain crucibles and heated above 700° C., then cooled and their solubilities determined. Upon heating to the above temperature, the Ag_3AsO_3 decomposed but the Ag_3AsO_4 remained unchanged. After remaining in the flasks for over 30 hours at room temperature, a sample of the solution from each flask was analyzed for silver and for arsenic. Table 9 shows the results of the tests.

TABLE 9.

No.	Material	Grams of Mat.	c.c. Vol. of Brine	g.p.l. Ag in Sol.	g.p.l. As in Sol.
1	Ag_3AsO_3	1 gr.	200	0.72	0.81
2	Ag_3AsO_3	2 gr.	200	0.82	1.73
3	Ag_3AsO_3 Heated above 700°C.	2	150	0.93	1.03
4	Ag_3AsO_4	2	150	0.95	1.36
5	Ag_3AsO_4 Heated	2	150	0.99	0.85

G. S. Forbes* performed experiments on the solubility of silver chloride in sodium chloride solutions. With a brine of NaCl concentration corresponding to that which is necessary to extract the lead (near saturation), he found that about from 0.7 grams of silver per liter to 1.0 grams per liter (varying with the concentration) might be dissolved by the brine before it

* G. S. Forbes, J. A. C. S. (1911) 33, 1937.

becomes saturated. Comparing the results of Table 9 with those of Forbes given above, the silver-arsenic compounds are found to be soluble to the extent that silver chloride is soluble. The silver arsenite and the silver arsenate react with the brine producing solid silver chloride, and hence the silver solubility should be expected to be the same as that of silver chloride in the same brine solution. These tests show that the formation during roasting of either silver arsenite or silver arsenate cannot account for the decreased silver extraction. Time was lacking in which to determine whether similar antimony compounds may cause a lowered silver extraction.

Conclusions on Leaching Oxidized Roasts.

From the experiments performed the following can be said concerning the use of brine containing ferric chloride in dissolving the lead and silver from oxidized roasts. First, the lead can be made readily soluble by roasting the ore above 600° C., at which temperature the lead is presumably sulphatized, and second, the silver extraction is decidedly lowered by roasting at high temperatures under the conditions of the tests; the reason for the decreased silver extraction cannot be definitely stated.

GENERAL SUMMARY.

In summarizing the results of the research investigation, the following conclusions may be drawn:

1. Almost complete precipitation of the lead may be effected by the use of an electrolytic cell.

2. By the use of a cell with an insoluble anode and a diaphragm to prevent mechanical mixing of the anolyte and catholyte, ferric chloride may be generated in the barren solution for use in further leaching operations.

3. With the low lead concentration of the pregnant solution, the catholyte must be vigorously agitated in order that a high current efficiency be maintained. The degree of agitation required is directly related to the current density.

4. By the use of the oxidized leaching solution the silver extraction from the chloridized calcine is materially improved. The lead extraction is not increased to any extent, it being already very high in brine containing no ferric chloride.

5. The brine containing ferric chloride will dissolve nearly 70 per cent of both the silver and the lead from the raw ore. The remaining 30 per cent occurs in insoluble compounds which cannot at present be identified.

6. By giving the ore an oxidizing roast at or above the sulphatizing temperatures (between 450° C. and 500° C.) the lead extraction is very high. However, upon roasting above 400° C. the silver extraction rapidly decreases. The reason for the decreased silver extraction from the oxidized roast has not been definitely determined.